Memory damping and energy-diffusion-controlled escape

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A recent refinement by Büttiker, Harris, and Landauer [Phys. Rev. B 28, 1268 (1983)] of Kramers's theory of activated escape at low damping is extended to the non-Markovian case with memory damping.

The dynamics of activated rate processes was treated first in a historic paper by Kramers.[1] Since that time, this important problem has been elaborated on many times resulting in several extensions of Kramers's original approach. In particular, we mention here the extension to a Markovian heat bath interaction described in terms of a master equation,[2-5] the work based on the concept of the mean first passage time in one-variable systems[6] and multidimensional systems,[7-11] the inclusion of physically relevant non-Markovian effects[12] at moderate and large damping[13,14] as well as the influence of non-Markovian damping on the extremely underdamped case.[15,16] In another set of papers, the problem of activated escape has been extended to various situations in nonthermal, driven multistable nonequilibrium systems.[17-20]

Our concern in this report is yet on another extension of Kramers's work for the underdamped case. Recently, an interesting refinement of Kramers's original approach for the underdamped case has been put forward by Büttiker, Harris, and Landauer[21] (BHL approach). Their theory extends Kramers's work for extremely low damping to the case of low-moderate damping; i.e., their theory interpolates between Kramers's result for moderate damping[1] and his result for extremely low damping. The goal of this work is the inclusion of physically relevant memory effects[12-16] into the BHL approach.

Important physical underdamped processes, being controlled by diffusion in energy space, are chemical reactions such as low-density unimolecular reactions, e.g., an isomerization reaction,[16] desorption processes of physisorbed species on surfaces,[15] or underdamped transport in Josephson junction circuits.[21,22] The memory effects become important in cases where the relevant coordinate of description is a molecular vibrational-type coordinate.[12,14-16] Then the correlation time associated with the heat bath motion is typically of the same order or longer than the relevant molecular vibrational period.

The starting point of our refinement is the energy diffusion Fokker-Planck equation of Zwanzig[16,23] and Carmeli and Nitzan,[15] which effectively does include memory effects (for details of the derivation see Refs. 15, 16, and 23):

$$\dot{p}_t(E)=\frac{\partial}{\partial E}\left[D(E)\left(\frac{\partial}{\partial E}+\beta\right)\nu(E)p_t(E)\right] . \tag{1}$$

Hereby, the frequency $\nu(E)$ is given in terms of the action variable J by

$$\nu(E)=dE/dJ . \tag{2}$$

$\beta=1/kT$ denotes the inverse temperature and $D(E)$ is the effective diffusion coefficient. $D(E)$ is determined by a correlation function expression,[16] or more explicitly, in terms of the memory damping $\gamma(\tau)$ and the Fourier components $\{x_n\}$ of the deterministic, undamped trajectory in the potential $V(x)$ (see Fig. 1)

$$x(J,\phi)=\sum_{n=-\infty}^{n=\infty} x_n(J)\exp(in\phi) \tag{3}$$

by[15] (M denotes the mass of the Brownian particle)

$$D(E)=\nu(E)2MkT\sum_{n=1}^{\infty} n^2|x_n|^2\int_0^{\infty}\gamma(\tau)\cos[n\nu(E)\tau]\,d\tau . \tag{4}$$

As a point of reference, in the Markovian limit with $\gamma(\tau)=2\gamma\delta(\tau)$, the diffusion coefficient $D(E)$ reduces to[1,15]

$$D^M(E)=J(E)\gamma kT . \tag{5}$$

At thermal equilibrium, the flux j_E along the energy coordinate

$$j_E=-D(E)\left(\frac{\partial}{\partial E}+\beta\right)\nu(E)\bar{p}(E) \tag{6}$$

vanishes. Thus, the equilibrium probability $\bar{p}(E)$ is given by

$$\bar{p}(E)=\frac{Z^{-1}}{\nu(E)}\exp(-\beta E) , \tag{7}$$

where Z denotes the normalization.

For the calculation of the rate we consider a situation as

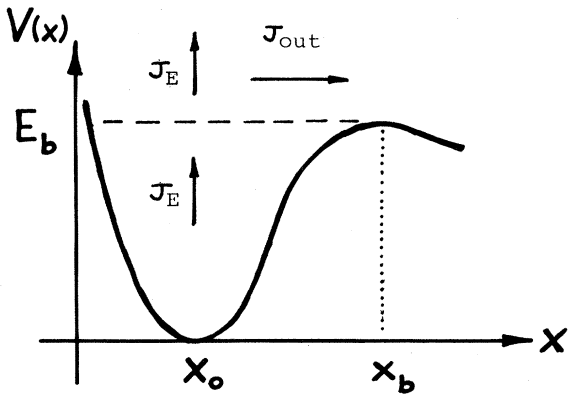

FIG. 1. Schematic sketch of the potential used in text. The diffusive flux along the energy coordinate is j_E and j_{out} is a horizontal outflow acting within a narrow energy region above E_b.

sketched in Fig. 1. We inject particles at the potential well and remove them the moment they reach the barrier E_b. The resulting nonequilibrium current j_E builds up a total integrated probability p_0 proportional to the escape time T:

$$j_E T = \int_0^{E_b} p_0(E)\, dE \ . \tag{8}$$

Using the ansatz

$$p_0(E) = \eta(E)\bar{p}(E) \ , \tag{9}$$

one finds from (6) for the nonequilibrium current

$$j_E = -D(E)\nu(E)\bar{p}\frac{\partial \eta}{\partial E} \ . \tag{10}$$

Integration of (10) from $E = E_1 \simeq kT$ to $E = E_b$ yields for the energy-independent current j_E, $E \leq E_b$,

$$j_E = [\eta(E_1) - \eta(E_b)] \Big/ \int_{E_1}^{E_b} \frac{dE}{D(E)\nu(E)\bar{p}(E)} \ . \tag{11a}$$

Observing that the integration in (11a) for deep wells is controlled by its upper integration limit, one obtains with $\eta(E_1) \simeq 1$

$$j_E = [1 - \eta(E_b)]D(E_b)\beta Z^{-1}\exp(-\beta E_b), \quad E \leq E_b \ . \tag{11b}$$

For energies $E > E_b$, we continue to allow a flux due to damping and fluctuations as determined by (6). Following the reasoning of Büttiker, Harris, and Landauer[21] we allow an outflow j_{out} from each energy range $(E,\ E + dE)$, $E \geq E_b$ (see Fig. 1); i.e.,[21]

$$dj_{\text{out}} = \alpha\nu(E)\eta(E)\bar{p}(E)\, dE \ . \tag{12}$$

In the steady state, this outflow is compensated by a divergence in the vertical flow up in energy

$$\frac{dj_E}{dE} = -\alpha\nu(E)\eta(E)\bar{p}(E) \ . \tag{13}$$

The parameter α measures the strength of the outflow. From a more physical point of view, the requirement of a finite outflow around a relatively narrow energy range above E_b [implying $\bar{p}(E) \neq 0$, $E \geq E_b$] models for low-moderate damping the adiabatic coupling of the energy variable to the relevant position coordinate. Inserting (10) into (13) and utilizing (7) one finds the equation

$$D(E)\frac{d^2\eta}{dE^2} + \left[\frac{dD(E)}{dE} - D(E)\beta\right]\frac{d\eta}{dE} - \alpha\eta = 0 \ . \tag{14}$$

Within the small energy range above E_b one can assume essentially a constant diffusion coefficient, i.e., $D(E) \simeq D(E_b)$, $dD(E)/dE \simeq 0$.

$$\eta(E) = c\exp(s\beta E), \quad s < 0 \tag{15}$$

yielding an exponentially decreasing density p_0 above E_b, solves (14). The physical solution follows from (14) as

$$s = -\frac{1}{2}\left[\left(1 + \frac{4\alpha}{D(E_b)\beta^2}\right)^{1/2} - 1\right] \ . \tag{16}$$

Setting $\eta(E) = \eta(E_b)\exp[s\beta(E - E_b)]$ and matching at energy E_b the constant current j_E in (11b) to the current determined from (10) for $E \geq E_b$ one obtains

$$\eta(E_b) = 1/(1 - s), \quad s < 0 \ . \tag{17}$$

If we substitute the solution for $\eta(E)$ into (11a) and utilize (8) and (11a) one finds for the rate $r = 1/T$

$$r = \frac{-s}{1-s}\left[\int_0^{E_b} \eta(E)\bar{p}(E)\, dE \int_{kT}^{E_b} \frac{dE}{D(E)\nu(E)\bar{p}(E)}\right]^{-1} \ . \tag{18}$$

For deep wells, the integrals in (18) can be evaluated within the harmonic approximation

$$\frac{\int_0^{E_b} \eta(E)\bar{p}(E)\, dE}{\beta D(E_b)\nu(E_b)\bar{p}(E_b)} = \frac{1}{\beta^2 D(E_b)\nu_0}\exp(\beta E_b) \ , \tag{19}$$

where ν_0 is the frequency in the potential well. Therefore, the result for the non-Markovian rate r for the underdamped case and deep wells reads

$$r = \left[\frac{(1 + 4\alpha/D(E_b)\beta^2)^{1/2} - 1}{(1 + 4\alpha/D(E_b)\beta^2)^{1/2} + 1}\right]\beta^2 D(E_b)\nu_0 \exp(-\beta E_b) \ . \tag{20}$$

The parameter α can be determined by use of computer simulations. Relying on the simulation results in Ref. 21, the appropriate value for the quantity α is around one. The result in (20) has the same structure as the result for white noise[21] which follows simply from (20) by substituting the Markovian limit $D^M(E) = J\gamma kT$, (5), for the non-Markovian diffusion coefficient $D(E)$, (4). Because in (18)

$$D(E) < kTJ(E)\int_0^{\infty} \gamma(\tau)\, d\tau \ ,$$

the influence of memory generally results in a *decrease of the prefactor* with increasing correlation time of the memory $\gamma(\tau)$. For a smooth barrier ( ) and for a cusp-shaped barrier ( ), the diffusion coefficient $D(E_b)$ occurring in (20) is readily evaluated: Note that for a smooth barrier $\nu(E_b) \simeq 0$; i.e.,

$$D(E_b) \equiv D_s(E_b) \simeq kTJ(E_b)\hat{\gamma}(\nu = 0)$$

[$\hat{\gamma}(\nu)$: one-sided cosine transform of $\gamma(\tau)$]; on the other hand, for a cusp-shaped barrier (truncated harmonic potential) $\nu(E_b) \simeq \nu_0$, i.e.,

$$D(E_b) \equiv D_c(E_b) \simeq kTJ(E_b)\hat{\gamma}(\nu_0) < D_s(E_b) \ .$$

For moderate-large damping,[14] the rate in (20) clearly becomes incorrect. A rate formula covering the whole damping regime could in principle be obtained by use of a fitting procedure between the current solutions of the corresponding two Fokker-Planck equations describing the corresponding diffusion regimes. Unfortunately, with an underlying two-dimensional phase-space dynamics [$(x,\dot{x})$ or (x,E)] such a fitting procedure *cannot be chosen uniquely.*

Note added. A bridging between the Kramers limits[1] (limit of white Gaussian noise) has been recently presented by Carmeli and Nitzan.[24] Moreover, a different treatment of this bridging has been put forward by Matkowsky, Schuss,

and Tier,[25] which overcomes an imperfection in Ref. 24 and is superior to the semibridging result of Büttiker, Harris, and Landauer,[21] which starts to fail within the moderate damping regime. Based on the concept put forward in Ref. 25, a useful approximation of the uniform rate expression r_{UNIF}, *in presence of memory damping,* is then given by

$$r_{\mathrm{UNIF}}=\left[\tau(E_b)+\frac{\omega_b}{\nu_0\mu}\exp\beta E_b\right]^{-1}, \tag{21}$$

with $\omega_b>0$ the (instable) angular frequency at the barrier, μ the memory-renormalized frequency evaluated in Refs. 13 and 14, and $\tau(E_b)$ the mean time to reach the barrier energy E_b as determined via the energy diffusion dynamics in Eqs. (1) and (4) (see Ref. 15).

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